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We report the experimental results on the performance of NIR tunable Cr⁴⁺-YAG Lasers, and laser spectroscopy, piezospectroscopy and photodynamics of Cr⁴⁺-doped Y₃Al₅O₁₂, Mg₂SiO₄ and Y₂SiO₅ crystals. The process of electron - phonon interaction in exciton migration and decay of population grating is discussed.

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**SPECTROSCOPIC STUDY OF NEW MATERIALS FOR NIR
SOLID STATE TUNABLE LASERS**

(Final Report)

Weiyi Jia and Huimin Liu

Period: Jan.1, 1992 to Dec.31, 1993

**U.S. ARMY RESEARCH OFFICE
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**UNIVERSITY OF PUERTO RICO, MAYAGÜEZ CAMPUS
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I. Foreword

Tunable solid state lasers have been developed rapidly and trend to replace dye lasers. One most successful example is Ti³⁺:sapphire lasers, the tunable range of which spans from 680 to 1100nm, to cover seven dye lasers' tuning range. Pico- and femto-second sapphire lasers have also been commercialized. The current research efforts are to expand the laser wavelength to the infrared, or to the blue-green and UV.

Following this direction, the substantial research work has been devoted to searching for new materials for the near infrared (NIR) solid state tunable lasers. Our two-year research project **Spectroscopic Study of New Materials for NIR Solid State Tunable Lasers** have been granted by the Army Research office. We feel that we have been very productive during the past two years of ARO support and have made important contribution to the above research field.

We would like to take this opportunity to thank the Army Research Office, Dr. Bob Guenther, Dr. Mikael Ciftan and all other officers for the financial support and advices. This is the first grant we got since we moved to the University of Puerto Rico-Mayaguez Campus in October of 1990 (Dr. Weiyi Jia) and in August of 1991 (Dr. Huimin Liu). Combined with other sources of external funding, we established Optical Materials and Laser Spectroscopy Laboratory, which allows us to be able to do quite competitive research work now. The lab is or will soon be equipped with cw, nano-, pico- and femto- second lasers, and with low temperature condition, and high uniaxial stress/pressure devices. We can be able to prepare optically activated sol-gel glasses. The spectroscopic wavelength can span from UV to the infrared (1.6 μm). Eleven papers have been or will soon be published under the auspices of ARO. All this achievement should be credited directly or indirectly to the Army Research Office.

We also would like to thank Dr. William Yen in the University of Georgia and Dr. Richard Powell in Oklahoma State University (now in Optical Center of the University of Arizona) for their hospitality to allow us to work in their laboratory. It is through the close collaboration, We could be able to complete our research project.

In the following, we present a brief introduction of our main results of research, which include three parts: Investigation on the performance of Cr-YAG lasers; Piezospectroscopic studies and photodynamics.

II. Performance of Cr-YAG lasers

We have studied the performance of Cr⁴⁺:YAG lasers, tunable over the range from 1.32 to 1.53 μm , under different operation regimes. Laser actions have been achieved by pumping with Nd:YAG lasers in Q-switched mode and cw mode and with a Cr,Nd:GsGG laser in the long pulse mode. Slope efficiencies up to 22% in the Q-switched pump mode have been obtained. The lowest threshold of 30 mJ was obtained for the long pulse pump mode. Excited state absorption and saturation absorption seem to limit the tuning range and the output characteristics. Such studies are believed to be important to improve the current Cr⁴⁺ laser materials and to search for new host materials and new lasing ions.

In the study of the laser performance, it was found that the laser output depended on the polarization of the pump laser beam relative to the crystallographic orientation of YAG rod. The observation leads to well understanding the relationship between the excitation saturation effect and the microstructure of electric dipoles of Cr⁴⁺ in YAG crystal. This eventually provides important information of how to use Cr-YAG crystals as passive Q-switch element.

2. Piezospectroscopic studies of Cr⁴⁺ doped crystals

Most of our effort in the past two years has been devoted to study the electronic energy level structures of Cr⁴⁺ in crystalline hosts. Three different materials have been studied: Cr-Mg₂SiO₅ (MSO), Cr-Y₃Al₅O₁₂ (Cr-YAG) and Cr-Y₂SiO₅ (Cr-YSO). Absorption, excitation and fluorescence spectra have been well studied. For example, Cr-YSO is a new material in which Cr ions are believed to be only in tetravalent state and to reside only in tetrahedral sites. The doublet of sharp lines in the near infrared is assigned to the pure electronic transition, and the broad band is the phonon sideband. However, it is difficult to tell if the transition originates from ³T₂ state or ¹E state. Some research groups assigned it as ¹E state transition, although this is in conflict with the results of lifetime and other measurements. The same arguments exist more or less to other two crystals.

In order to clarify the energy level structures of Cr⁴⁺ in different crystal hosts, stress dependence experiments were performed at 10 K using a novel stress device designed by us. Large stress-induced energy shifts of the zero phonon lines of the fluorescence were found in the order of 10 to 20 $\text{cm}^{-1}/\text{kbar}$ in all of the crystals. It is concluded from the large stress effects that the emission of the sharp lines and the broad phonon sideband originate from one of the orbital components of ³T₂ state of Cr⁴⁺ but not from ¹E state or a mixture state of ¹E and ³T₂.

The shift rates of the spectra with stress were found to very

much depend on the relative orientation of the crystal to the stress. The information helps us to identify the occupation of Cr⁴⁺. We believe, for example, in the case of Cr-forsterite, Cr⁴⁺ replaced Si in tetrahedral sites but not reside in tetrahedral voids.

In addition, pseudo-spectral splitting were observed in all three crystals. These splittings are ascribed to the reduction of the crystal symmetry induced by uniaxial stress when it is applied not parallel to the crystallographic axes. An analysis based on group theory is presented. The result again help us to clarify the site occupation of Cr⁴⁺ in the crystal host.

Based on the confirmed energy level structure, we are able to analyze the radiative and nonradiative decay processes of Cr⁴⁺ in these crystals. We believe we obtained a profounder understanding of both spectroscopy and dynamics in the laser materials.

3. Dynamics of excited states

Dynamic processes of excited states of Cr doped forsterite samples with different concentration ratios of Cr⁴⁺/Cr³⁺ and a purely Cr⁴⁺ doped CGS sample were studied by degenerate four wave mixing technique. A slow ns scattering signal and a fast ps signal were observed. The slow signals observed in all the samples are identified to be from the established transient Cr⁴⁺ population grating. The fast ps signals are quite strong in the sample with higher Cr³⁺ concentration, faded out in the low Cr³⁺ concentration sample, and disappeared in the pure Cr^{4+:}CGS sample. This may imply existence of a fast nonradiative energy transfer from Cr³⁺ to Cr⁴⁺ within 50 ps. Some combination phonon modes of octahedral (Cr³⁺) and tetrahedral (Cr⁴⁺) vibrations may get involved in the electron-phonon coupling process. Our result is in good agreement with the recent experimental observation by Demos et al. In their time resolved Raman scattering experiment, the phonon lifetime between 40-50 ps was found to be involved in the nonradiative decay of tetravalent Cr in forsterite.

Dispersive properties of population grating in Cr doped YAG crystal has been also studied by four wave mixing with a cw dye laser pumped by an Ar laser. It was found that, in the millisecond time scale, Cr³⁺ coexisted in the sample with Cr⁴⁺ plays a dominate role in the creation of the grating at room temperature. The result is ascribed to the much longer life time (1 ms) of Cr³⁺ than that (3 μ s) of Cr⁴⁺.

In addition, in order to deeply understand the role of nonequilibrium phonons which are commonly created in sideband pump in the tunable laser materials, we studied photodynamic process in the one-dimensional antiferromagnet CsMnCl₂.2D₂O. We observed nonequilibrium phonon assisted exciton migration, which lead to

different exciton decays when the phonon sideband and pure electronic line were pumped respectively. The finding may shed a new light on understanding the important role of the nonequilibrium phonons produced in sideband pumping in tunable laser materials. This part of research is just initiated and will be continued in the future proposal.

III. Publications

1. Weiyi Jia, H. Eilers, W. M. Dennis, W. M. Yen, and A. V. Shestakov, "Performance of a Cr⁴⁺:YAG Laser in the Near Infrared", OSA Proceeding on Advanced Solid State Lasers Vol. 13, 31 (1992).
2. Weiyi Jia and W. M. Yen, "Spectroscopy of a New Lasing Ion Cr⁴⁺ for NIR Solid State Tunable Lasers" (in Chinese, not submitted to ARO), in book "Advances in Luminescence" ed. by Fan Xiwu and Ge Shichao, Scientific Press, Beijing, China, 1992, p38.
3. U. Hömmerrich, H. Eilers, S. M. Jacobsen, W. M. Yen, W. Jia and Y. Wang, "Spectroscopic Investigation of the NIR Center in Cr-Doped Y₃SiO₅", OSA Proceeding on Solid State Lasers, Vol 15 (1993) 441.
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10. U. Hömmerich, H. Eilers, W.M. Yen, W. Jia and Y. Wang,
"Effects of Uniaxial Stress on the Metastable Level in
 $\text{Cr}^{4+}:\text{Y}_3\text{SiO}_5$ ", Optics Letter, accepted.
11. H. Eilers, U. Hömmerich, S.M. Jacobsen, W.M. Yen, K.R. Hoffman
and W. Jia, "Spectroscopy and Dynamics of $\text{Cr}^{4+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ ", Phys.
Rev. in press, 1993.

IV. Participating Scientific Personnel

Dr. Weiyi Jia, Principle Investigator, Associate professor;
Dr. Huimin Liu, co-investigator, Associate professor;
Ms. Yanyun Wang, Research Associate;

Mr. Juan Daniel Romero-Chong
Master degree student
Thesis Title: Dispersive response of Population grating
of Cr doped YAG crystal By Four Wave Mixing.
To be graduated in June of 1994.